

# Multifunctional 2D- Materials: Selenides and Halides

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Novel materials Bring Revolution for Devices and hence systems

# Multifunctional 2D- Materials: Selenides and Halides

## Objectives:

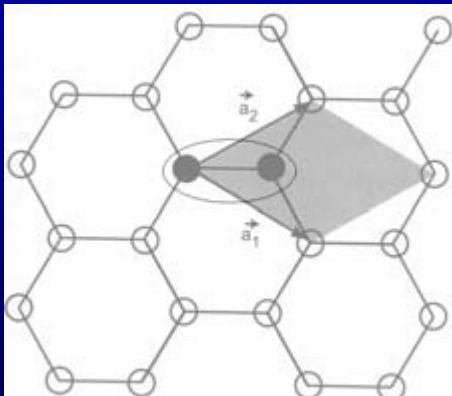
The main objective is to introduce some new multifunctional 2D materials and compare their performance with bulk, thin film, micro and nano crystals

Novel materials Bring Revolution for Devices and hence systems

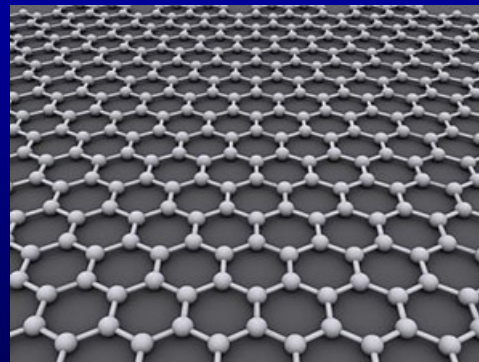
# Huge number of papers have been published

## Where are big bang applications.....?

- Since the isolation of graphene, a single-layer of graphite, in 2004, a large amount of research has been directed at isolating other 2D materials due to their unusual characteristics
- Applications such as photovoltaics, semiconductors, electrodes and water purification.
- It is a source of remarkable properties, such as very high electronic conductivity and mobility.
- Its breaking strength is 200 times greater than steel.



Lattice structure of graphene  
in real space

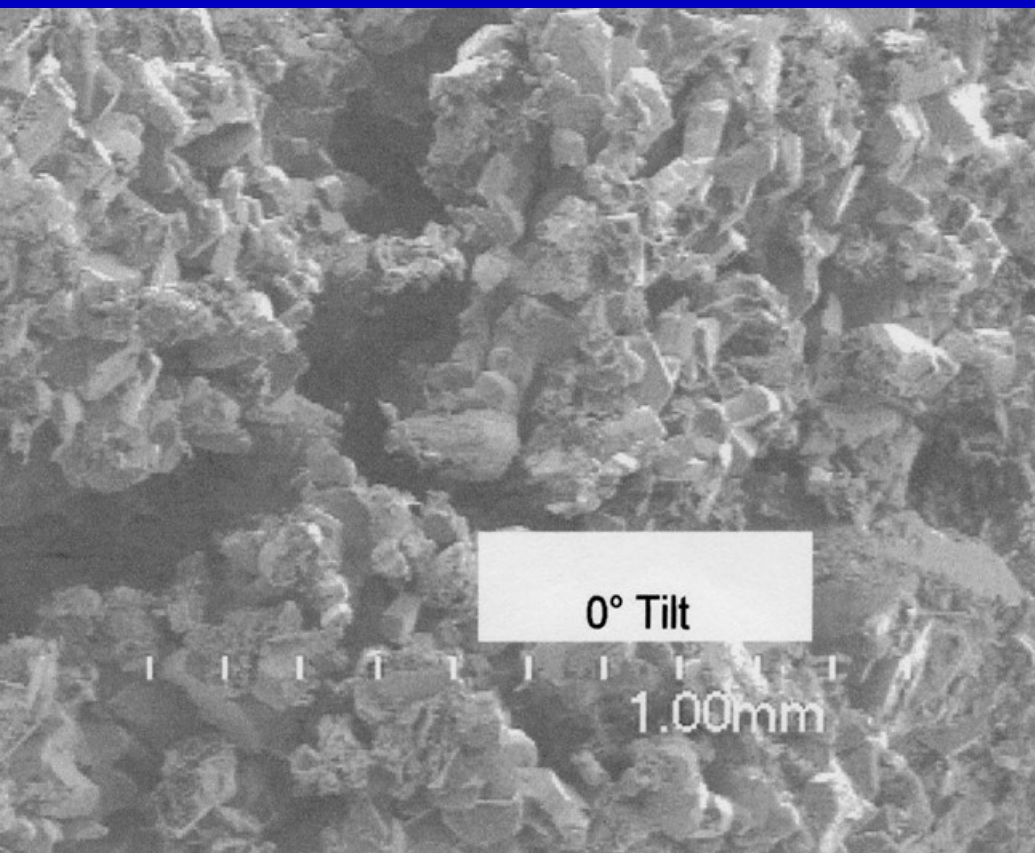


The atomic arrangements  
are in honeycomb mode in  
graphene

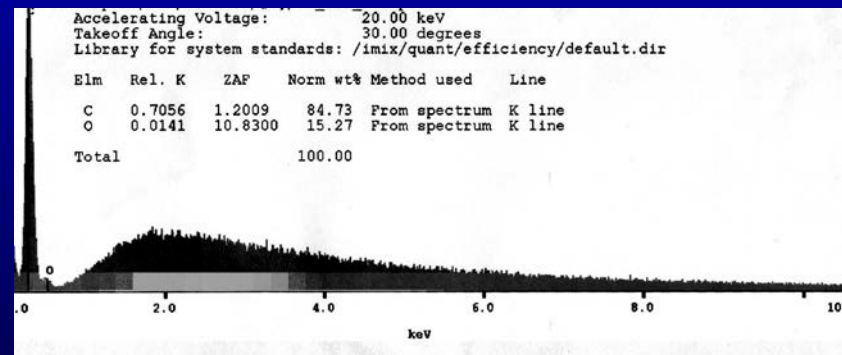
## Applications ?

*2D structures were known in materials and were referred as layered materials*

# We have grown and characterized morphology and composition of wrinkled multi layer sample of Graphene



Traces of oxygen was determined because annealing of SiC was performed in unevaluated furnace



*Singh et al (unpublished) other 2D crystals can be fabricated into devices*

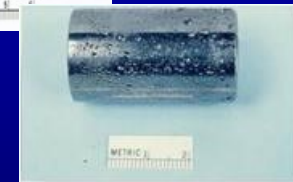
# Motivation for Selenide Crystals

Enables scaling of power and spectral range

- Transparency from 0.6 to 20  $\mu\text{m}$
- Extremely low intrinsic absorption ( $\leq 0.001 \text{ cm}^{-1}$  from 1 to 16  $\mu\text{m}$ )
- Large “ $d_{\text{eff}}$ ” coefficient

## Bulk Materials

- Binary Selenide Crystals; GaSe (GSe)
- Ternary Selenide Crystals;  $\text{Ti}_3\text{AsSe}_3$  (TAS)
- Quaternary Selenide Crystals;  $\text{Ag GaGe}_3\text{Se}_7$  (AGGSe)



## Quassi Phase Matched Materials

- Zinc Selenide Crystals



## Laser Host Materials

- Halide based laser host (Lead Bromide)

# Selenides have huge potential for device applications and have lowest absorption coefficient in wide transparency range

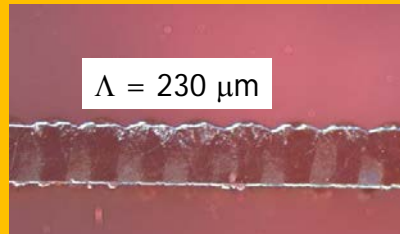
Optoelectronic devices, LEDs, Solar cells, sensors, Laser diodes, THz sensors

Substrates and transparent electrodes

High power RF and electronic devices and components

## Applications of Selenides

Self compensating gas sensors



Lasers and Optical pumping

Piezoelectric and pyroelectric devices

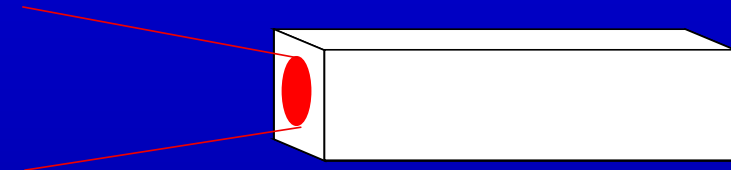
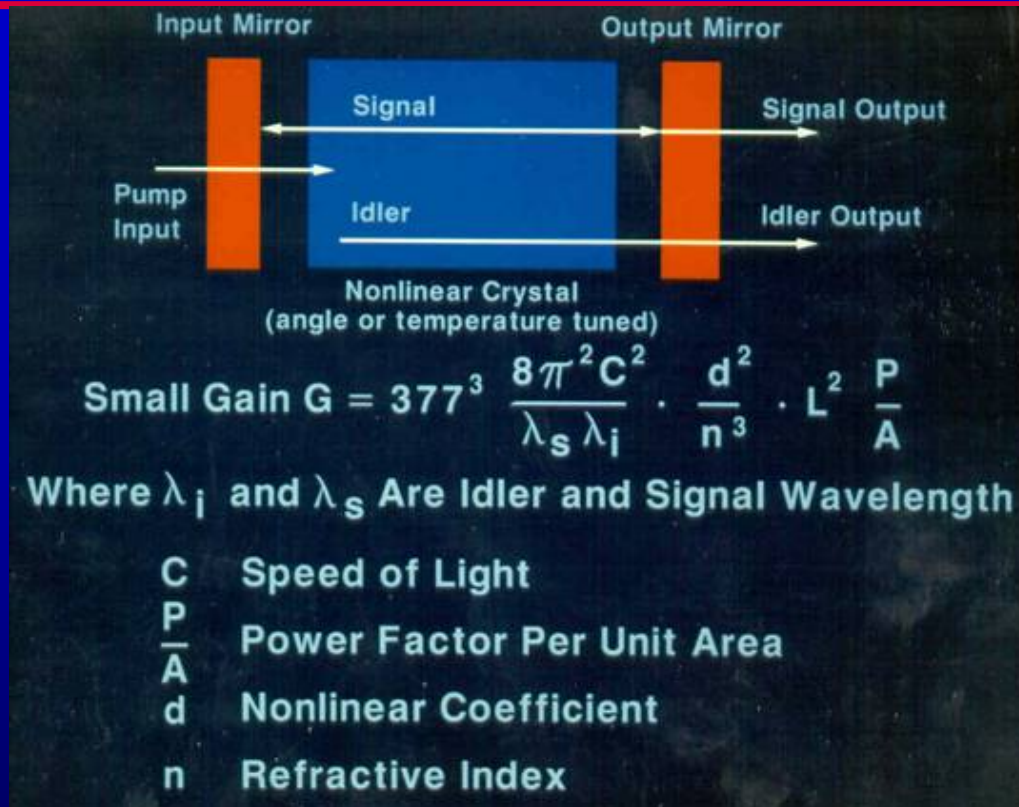
**Bulk, thin film, nano and QPM off II-VI compounds have potential**

SAW devices such as filters, oscillators

Electronic FETs



# NLO Requirements for direct pumping by 1.06 $\mu\text{m}$ laser



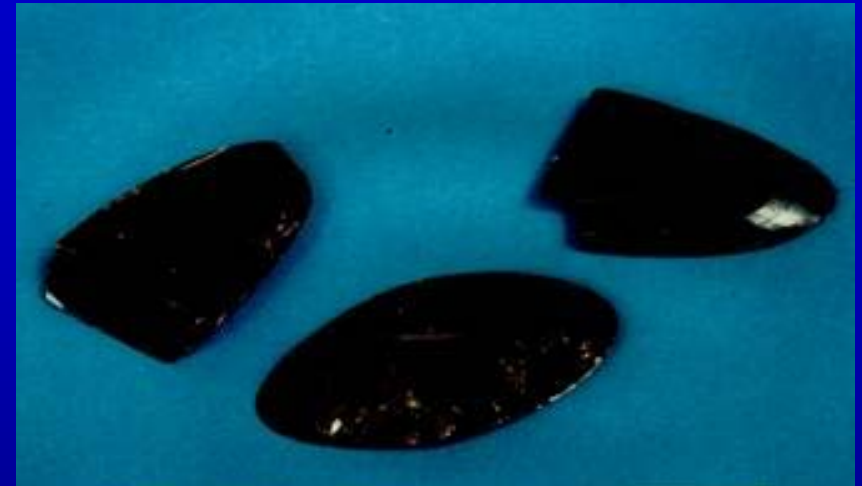
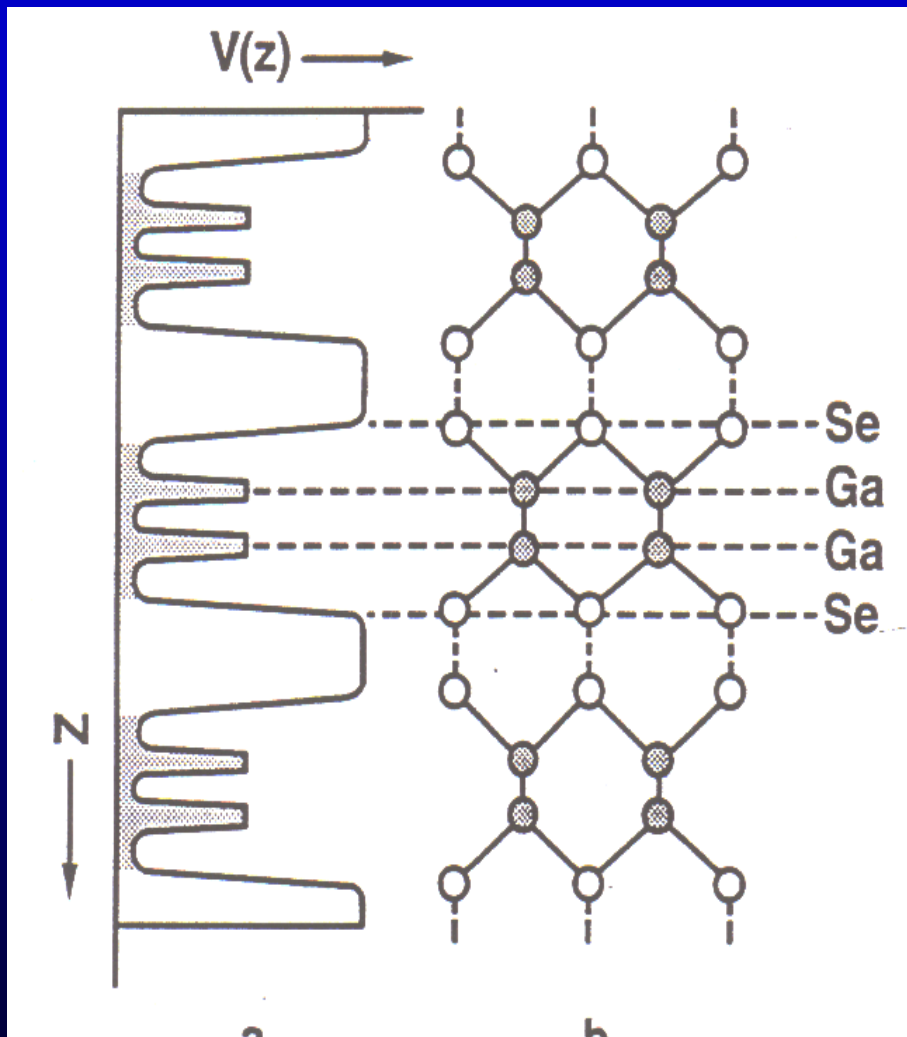
Birefringent Materials and  
Required characteristics

## Benefits of Ag-Ga-Ge-Se System

- Damage T-hold  $> 3 \text{ J/cm}^2$
- Small Walk-off
- High  $d^2/n^3$  (180)
- Low cost
- Adhering coatings
- Transparency 0.65 to 18  $\mu\text{m}$

Transparency range can be designed by Selenium

# Why New Derivatives? Very weak bonding along C direction causes cleaving



Layered structures along - c and covalent along -a direction



**GaSe is a very good fabricable 2D material.**

**Phase diagram shows two congruent compounds**

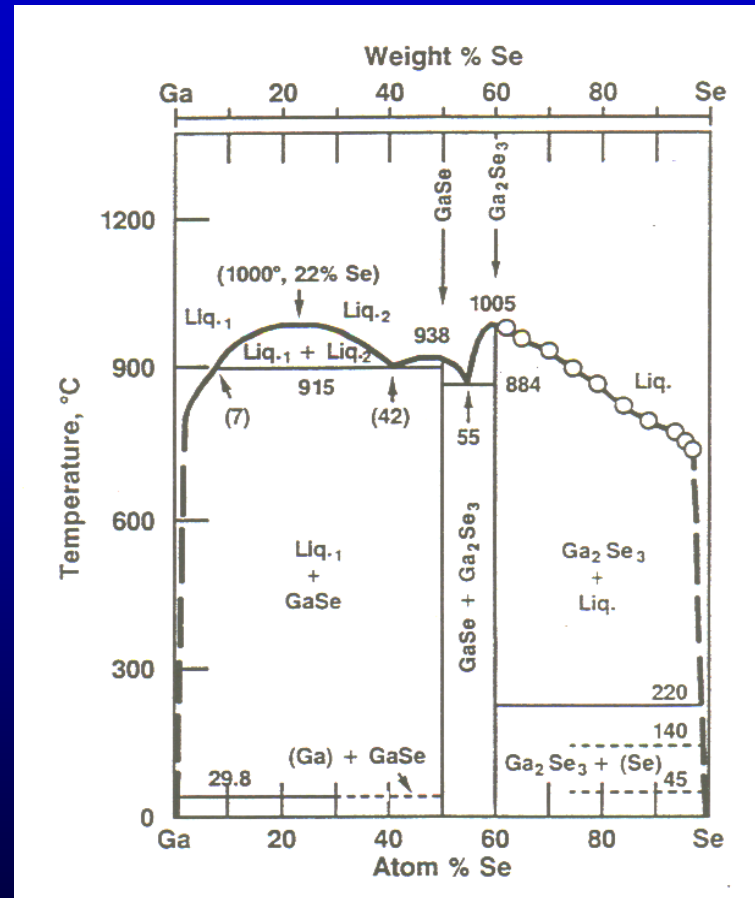
- GaSe is a congruent compound which melts at 938C.

- Charge for crystal growth was prepared by combining Ga and Se

- Both Ga and Se were further purified before reacting

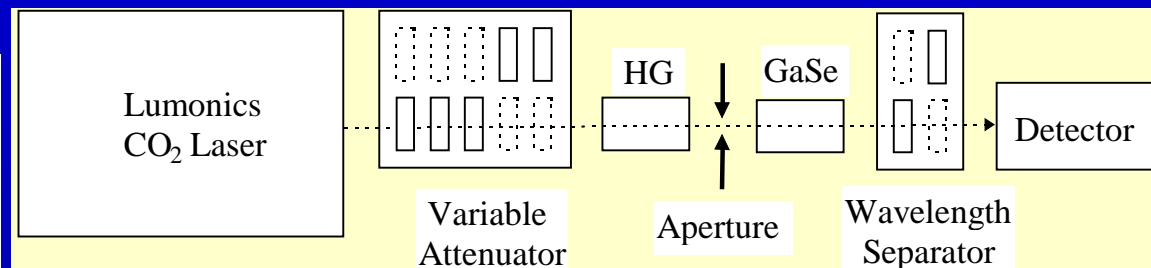
- Crystals were grown in Bridgman geometry

- In and other dopants were used in GaSe

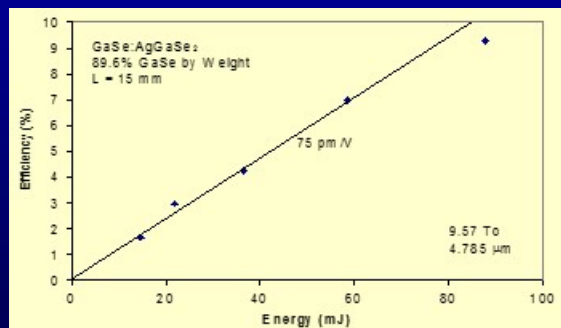
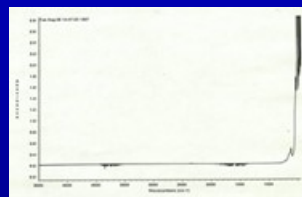
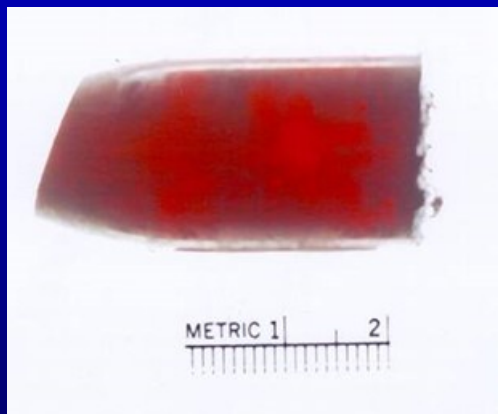


**There are congruent compositions in Ga-Se system**

# Pure GaSe has very large NLO Merit ( $d^2/n^3$ ) but peels like mica when fabricated



Lumonics 203 CO<sub>2</sub> laser on 9P(22) at 9.569 mm  
 Fundamental intensity varied with attenuators  
 Output measured with pyroelectric detector  
 Second harmonic produced with TAS crystal  
 Third, fourth, and OPO mixing in GaSe crystal  
 SHG also measured directly in GaSe



Oscillator: 100 mJ/Pulse

9.25 mm, 20 nsec FWHM

~ 100 mJ/Pulse, < 50 kHz

Amplifier: ~10 dB Gain

~ 1 mJ/Pulse, < 50 Watts

Procedure: Focus to 150 μm spot in crystal, and measure 9.25 and 4.625 μm power using sapphire plate to block fundamental

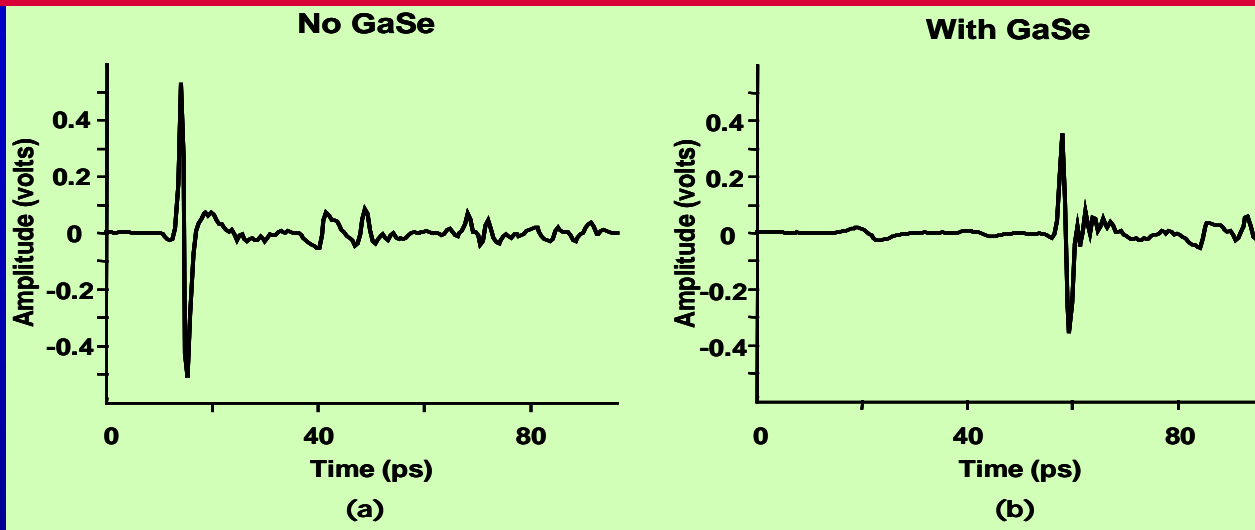
Pure GaSe showed “d” coefficient up to 75pm/V

\* >3.7 J/cm<sup>2</sup> at 9.25 mm and 20 nsec pulses (>180 MW/cm<sup>2</sup>)

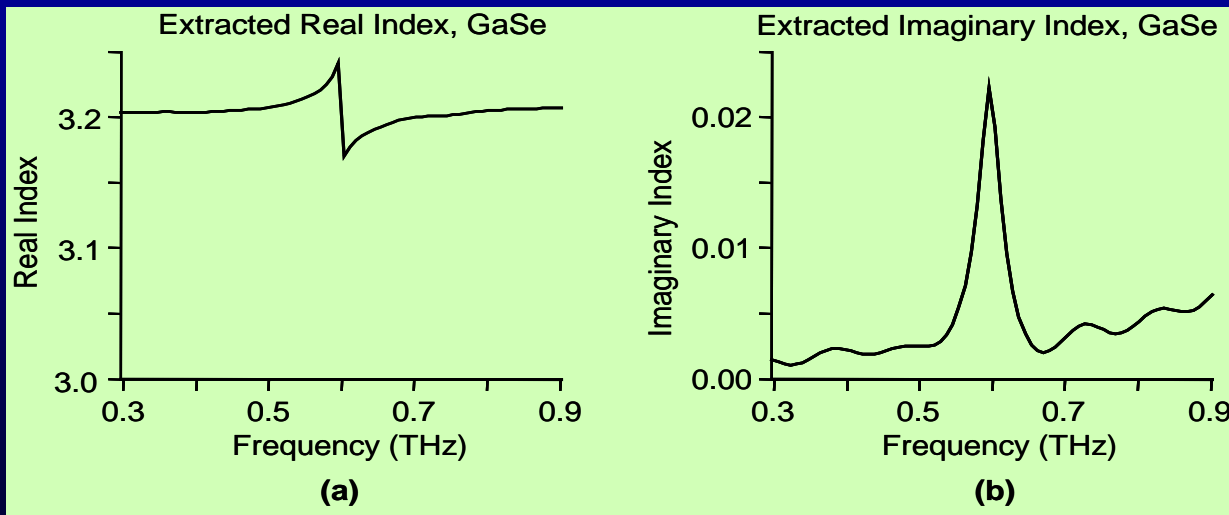
\* >86 kW/cm<sup>2</sup> average power at 9.25mm

**GaSe has strong cleavage, “d” is significantly reduced in doped GaSe**

# GaSe is an excellent THz sensor material



Terahertz waveforms: (a) without and (b) with the GaSe sample



Index of refraction extracted from transmission measurements of GaSe (a) real part (b) imaginary part. The y-scale of the real index spans a range of 0.25, while the imaginary index spans a range of only 0.025.

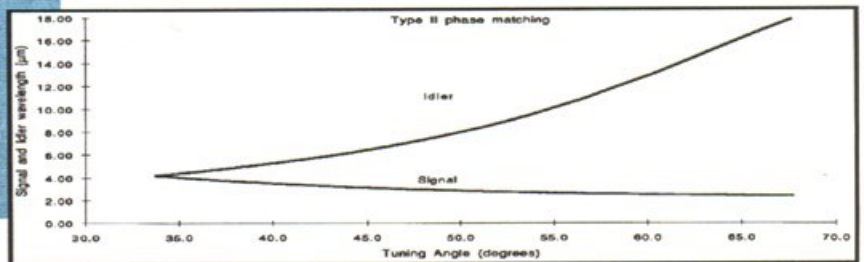
# GaSe Crystal is can be considered as a bundle of layers



**GaSe Cleaved Crystal**



**GaSe Charge**

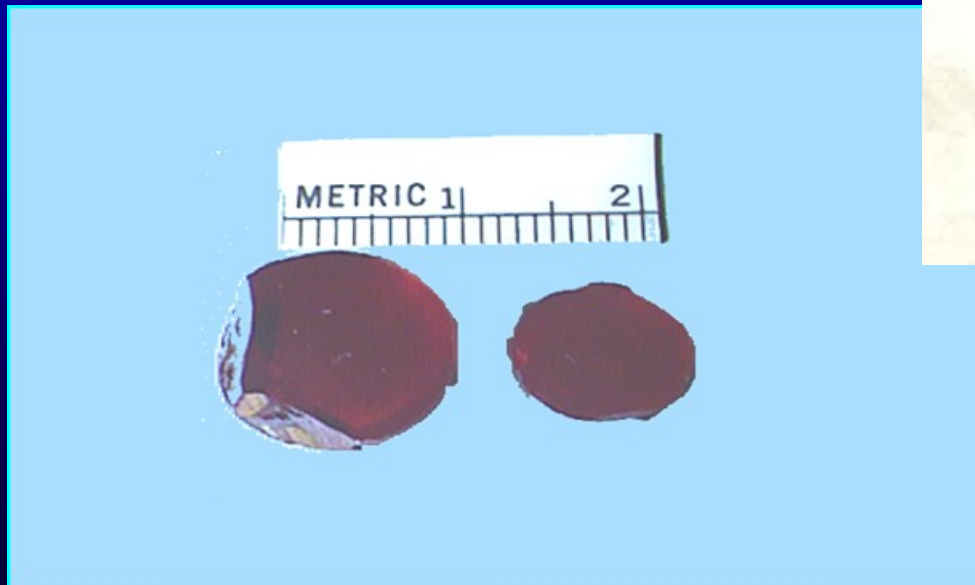


**Tuning Curve**

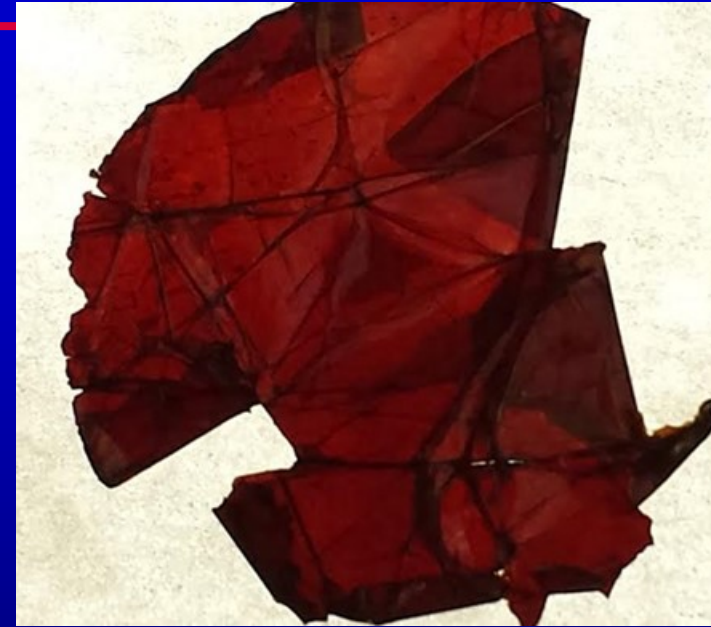
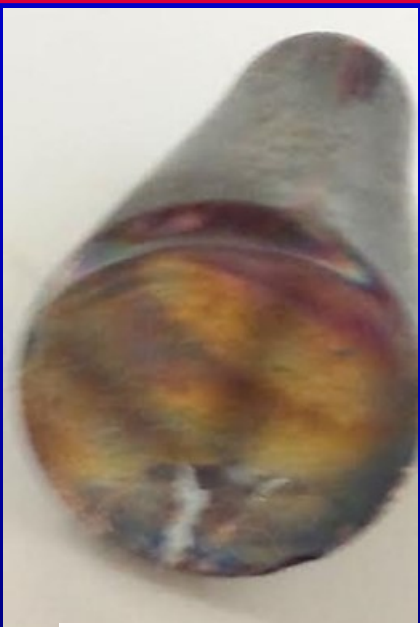
**GaSe composition showed phase matching**



# Thallium gallium selenide is another material with layered structures



# Extremely thin layer of Gallium Selenide

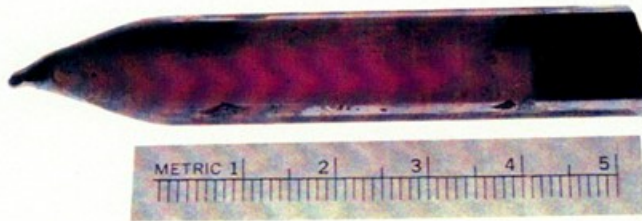


Cleavage plane is visible in pure crystal.

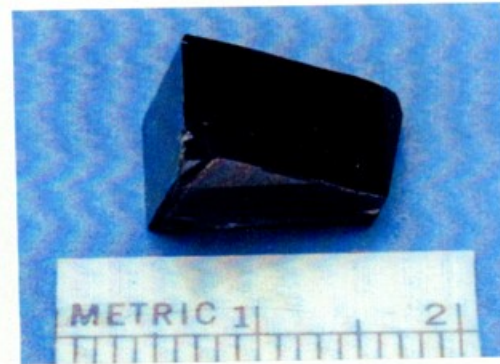
Doped crystals increase forces between Vander Waal bonds



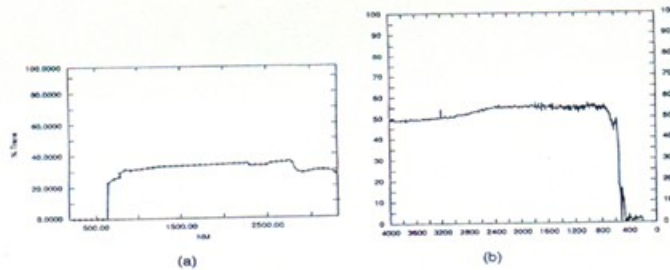
# Gallium Selenide for NLO Applications



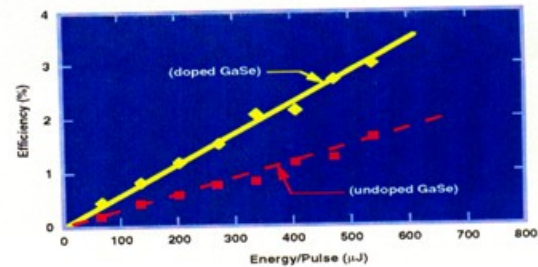
As-grown GaSe



GaSe prism



Transmission curve for uncoated GaSe in (a) Near-IR, and (b) Far-IR wavelength region



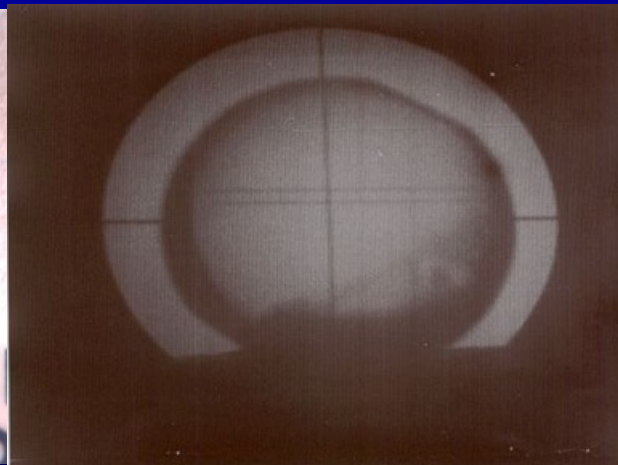
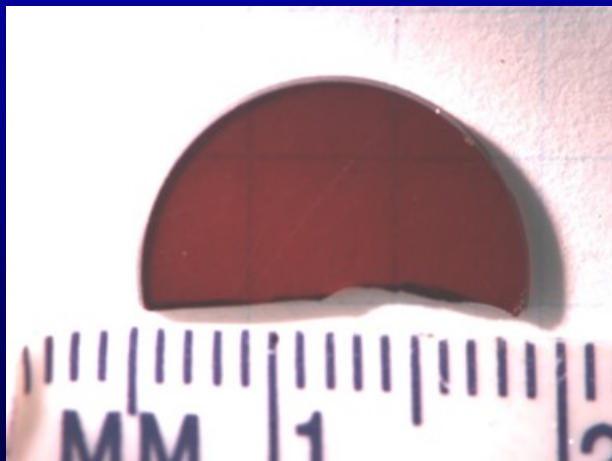
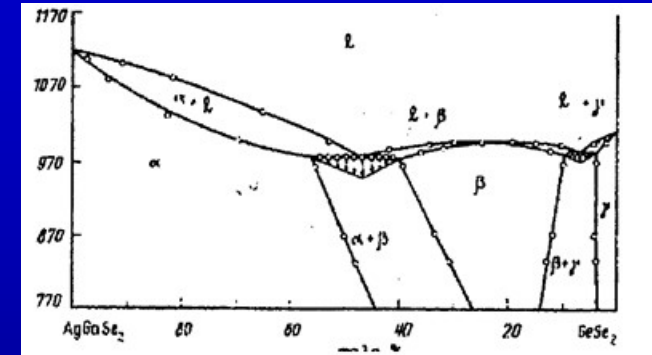
SHG output of 4 mm GaSe samples

Performance of modified material: We doped with Indium

# AgGaGe<sub>3</sub> Se<sub>8</sub> Crystals were synthesized and grown for SHG demonstration

Three members of AgGaGe<sub>n</sub> Se<sub>(2n+2)</sub> family are studied and some data available in literature:

- AgGaGeSe<sub>4</sub>
- AgGaGe<sub>3</sub> Se<sub>8</sub>
- AgGaGe<sub>5</sub> Se<sub>12</sub>

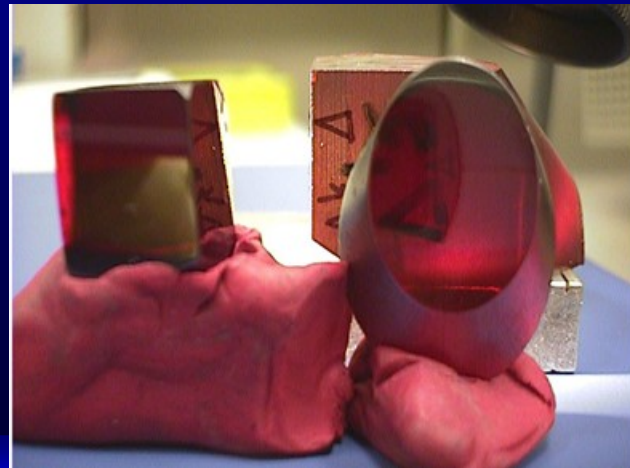


Quaternary 2D materials were slightly stronger in -C direction

# **AgGaGe<sub>3</sub>Se<sub>8</sub> Crystal Could be grown and fabricated due to stronger Vander Waal bonds**



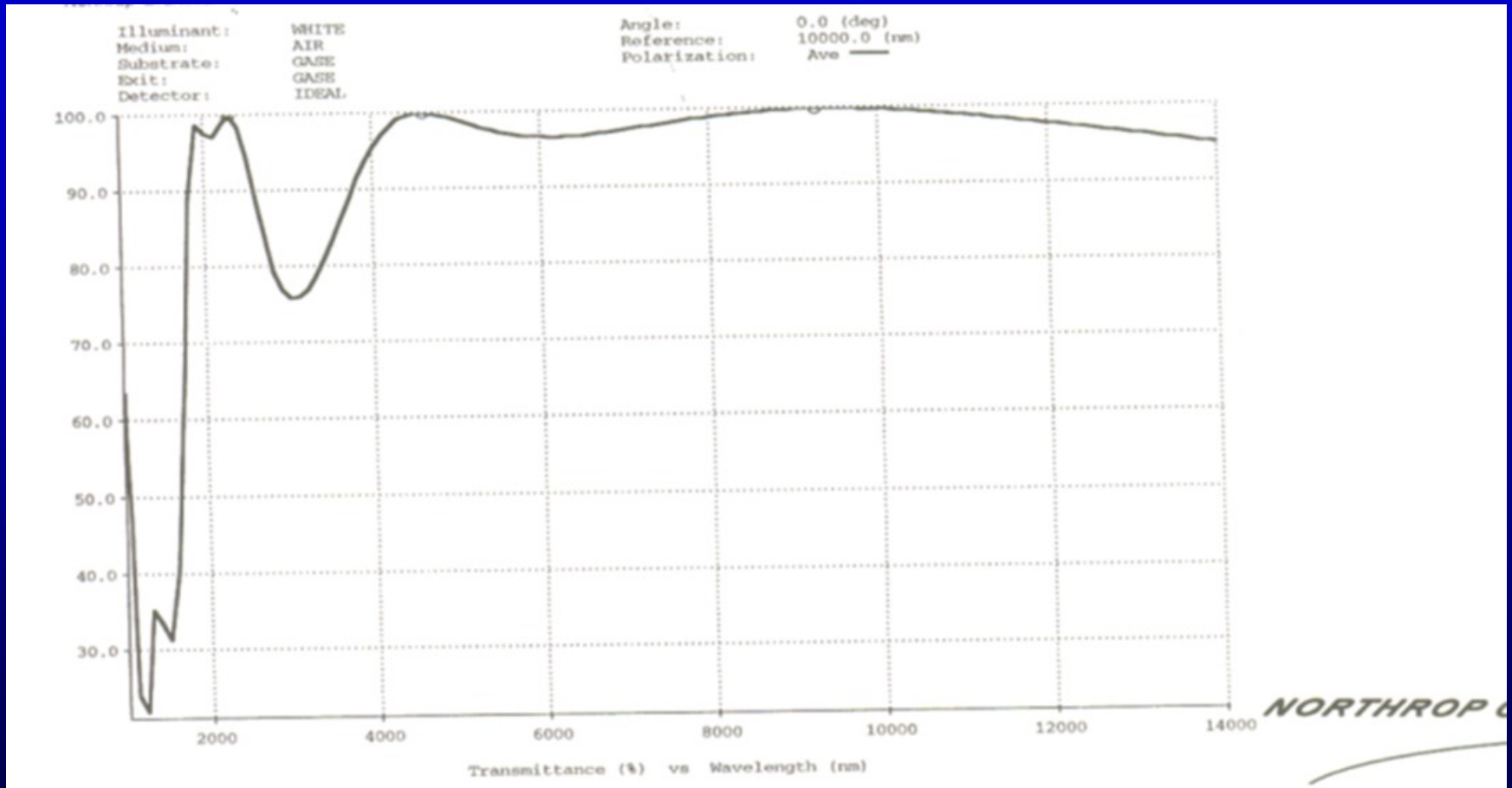
As-grown crystals were up to 6 cm long



Single crystals were grown by Bridgman method

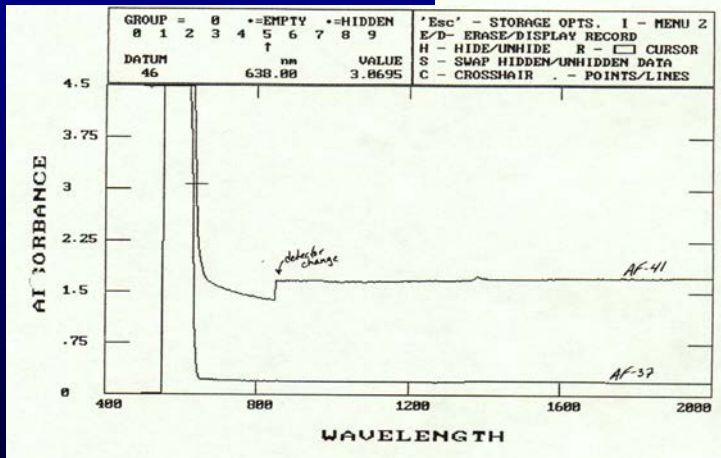
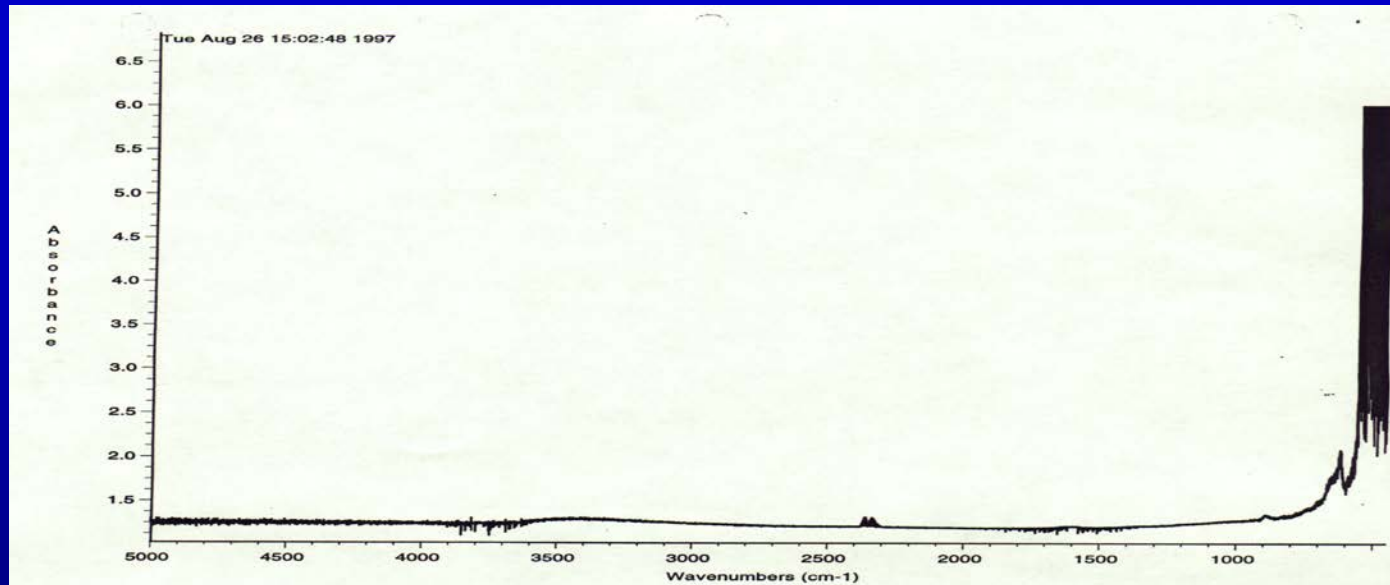


# Gallium Selenide



**Wide transparency range AR coatings**

# Gallium Selenide and its derivatives have lowest absorption

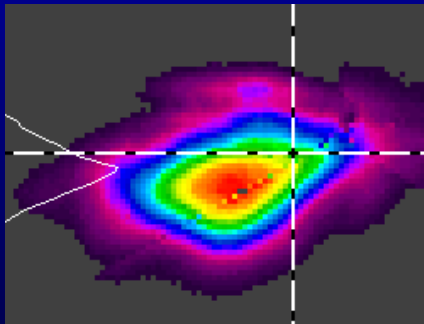
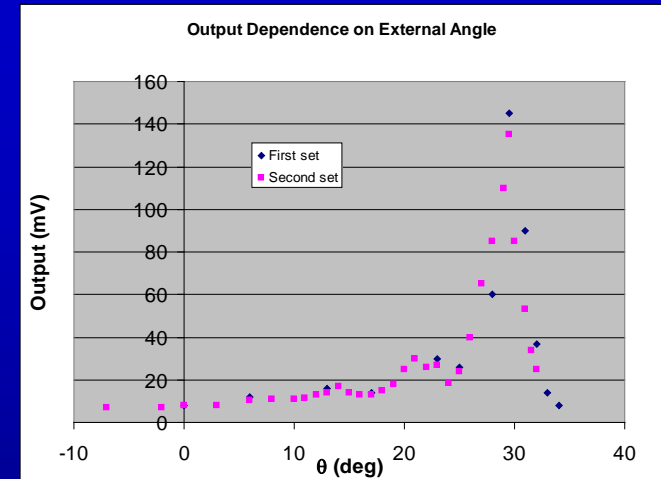


Lowest absorption in any optical NLO, THZ crystal

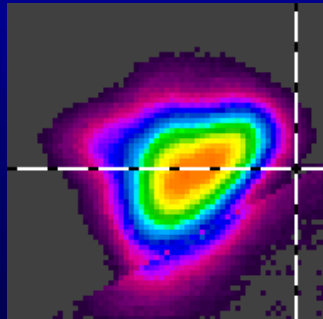
# Experimental Observations and Measured Signals

- Sample transmits beam with very low scattering
- Possibly higher damage threshold than previous selenide samples
- Optical transmission seems good, especially if we compare to expected Fresnel losses for AgGaSe<sub>2</sub> (about 19% per face)
- Transmission measured for different yaw, pitch angles; last row shows where obtained greatest NLO signal; lower transmission and degraded beam image shows probable beam clipping.

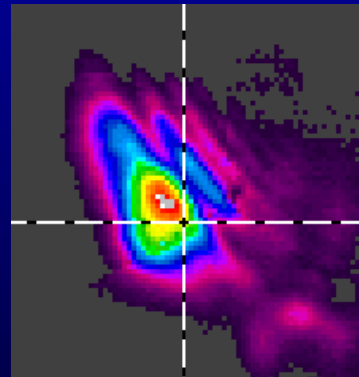
$\phi$ (deg)	$\theta$ (deg)	Transmission
0	0	0.64
10	0	0.67
10	30	0.51



Incident beam, 9.27  $\mu\text{m}$



Transmitted 9.27  $\mu\text{m}$ ,  
 $\phi \approx 10^\circ$ ,  $\theta \approx 0^\circ$   
external angles



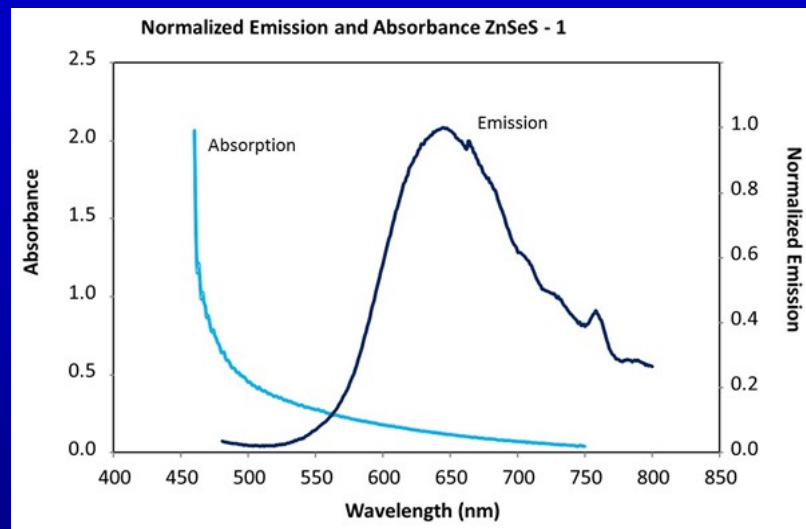
Transmitted 9.27  $\mu\text{m}$ ,  
 $\phi \approx 10^\circ$ ,  $\theta \approx 30^\circ$   
external angles

- Appears partially limited by aperture since peak of signal observed at  $\sim 30^\circ$  off normal incidence (see image previous slide)
- Walkoff: for AgGaSe<sub>2</sub> and 9.27  $\mu\text{m} \rightarrow 4.63 \mu\text{m} + 4.63 \mu\text{m}$  SHG interaction walkoff angle is 12.45 mrad
  - This gives  $l_a = 1.4 \text{ cm}$  aperture length, slightly below actual 1.5 cm length of crystal
- From SNLO, AgGaSe<sub>2</sub> angular tolerance is 14.33 mrad-cm (half-width to zero), so expected (external) acceptance angle for this crystal length is  $1.1^\circ$ , which is close to the measured value of  $1.5^\circ$ .

**Sample showed low scattering. "d"  
= 30pm/V**

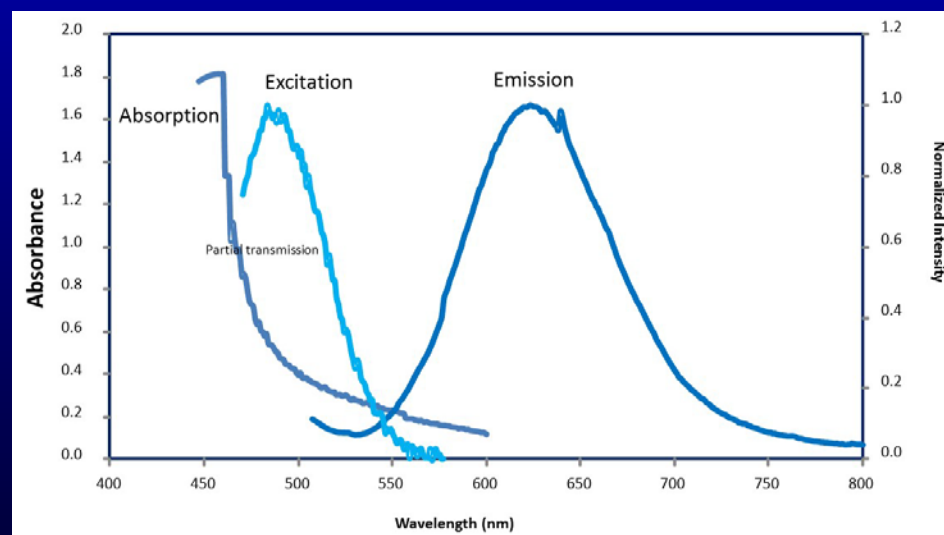


# Spectral characteristics of ZnSeS



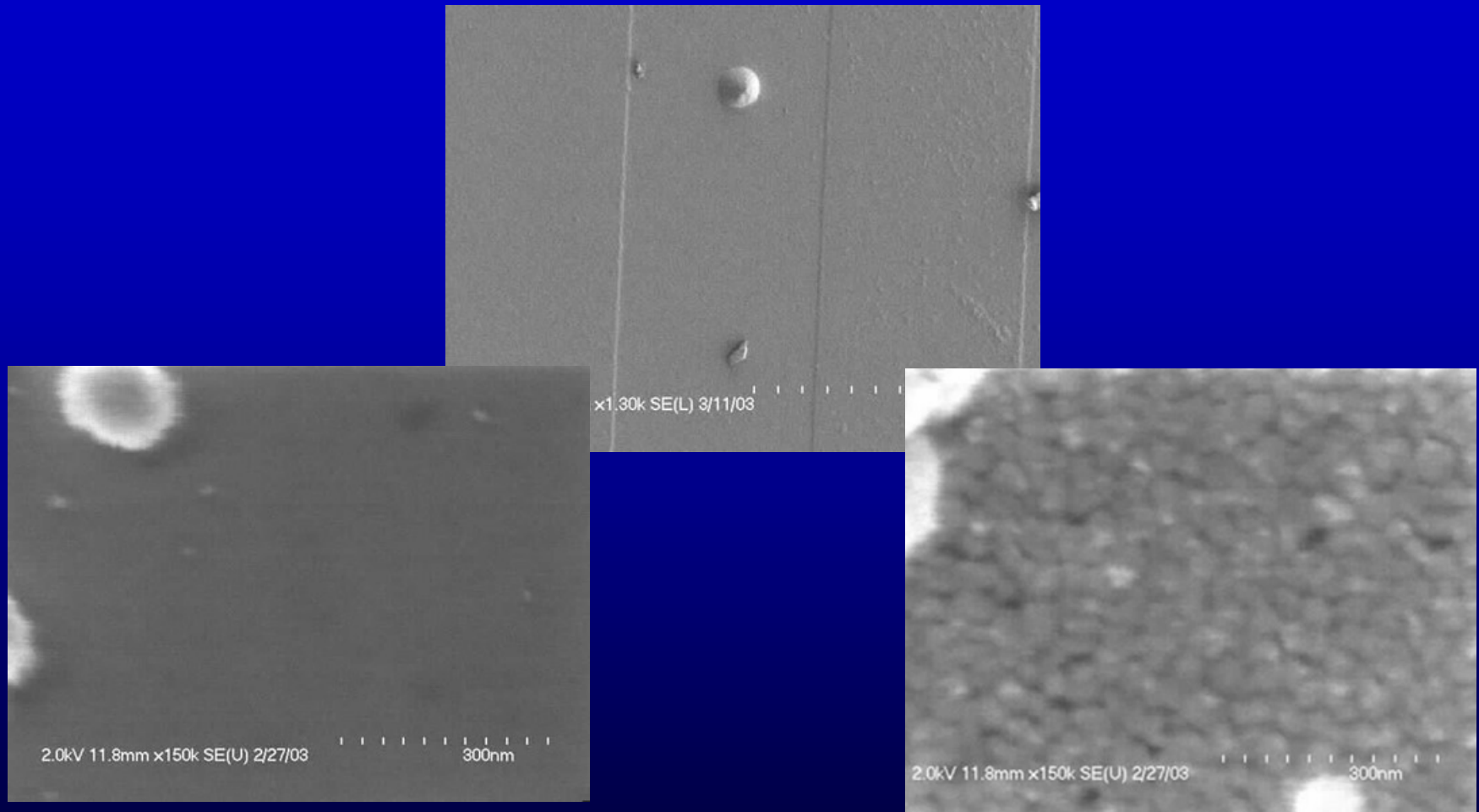
Normalized absorbance and emission spectra with ZnSeS-1. The overlapped region occurs between 450 and 550 nm (2.70eV) with emission maximum near 610-630 nm.

The data of crystal ZnSeS-2 shows detailed absorption, excitation and emission spectra without filter similar to that of crystal ZnSeS-1.



There are congruent compositions in ZnSe system

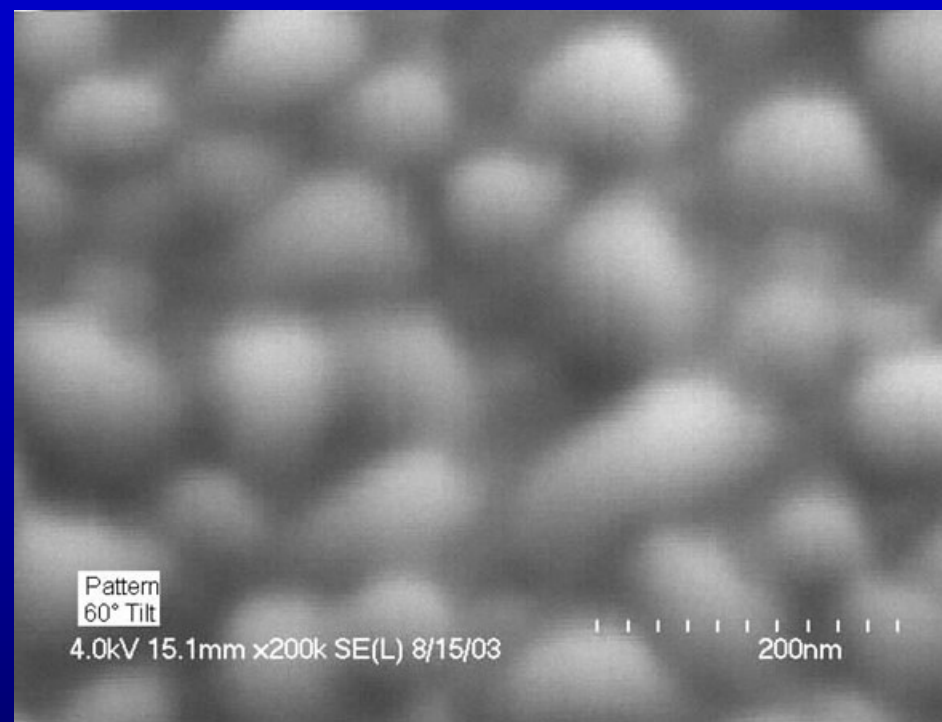
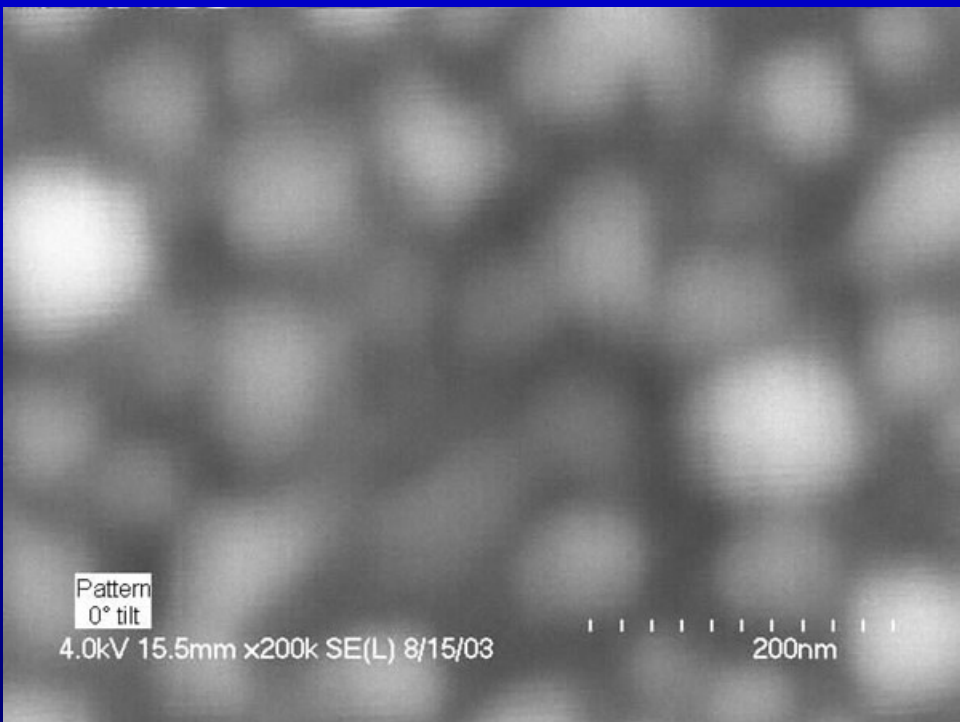
# Nanomorphology of ZnSe on patterned and unpatterned substrates



Morphology of (a) ZnSe on patterned and non-patterned portions of substrate (b) epitaxial and smooth film on non-patterned GaAs and (c ) nano particles of ZnSe on patterned substrate

*Materials are based on strategic requirements of DoD, DHS and DoE*

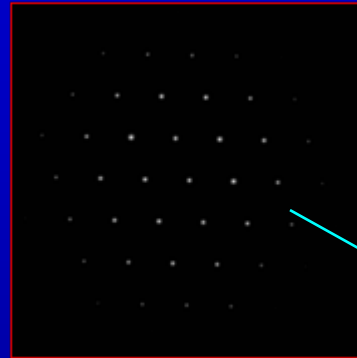
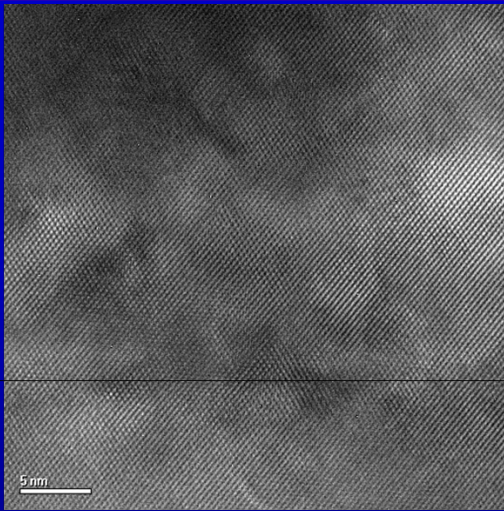
# Morphology of nanolayers



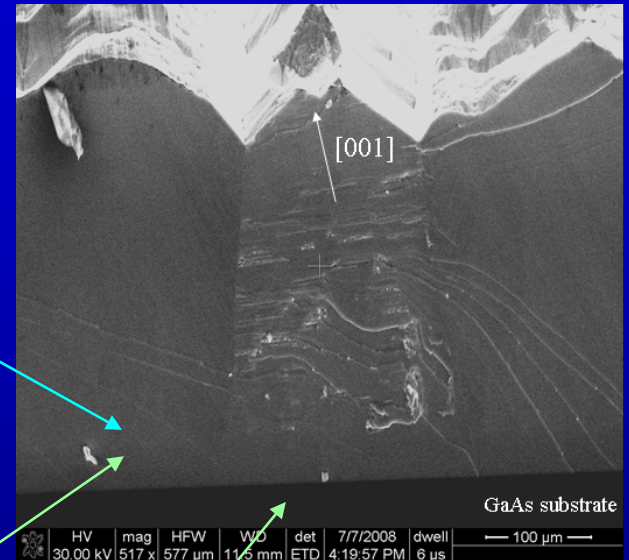
Morphology of nano particles of ZnSe at viewing angles of 0 and 60 degree tilts indicating that particles are spherical

*There was very small difference in nanomorphology of ZnSe layers*

# Electron Microscopy of (110) Confirms Orientation and Elemental Composition

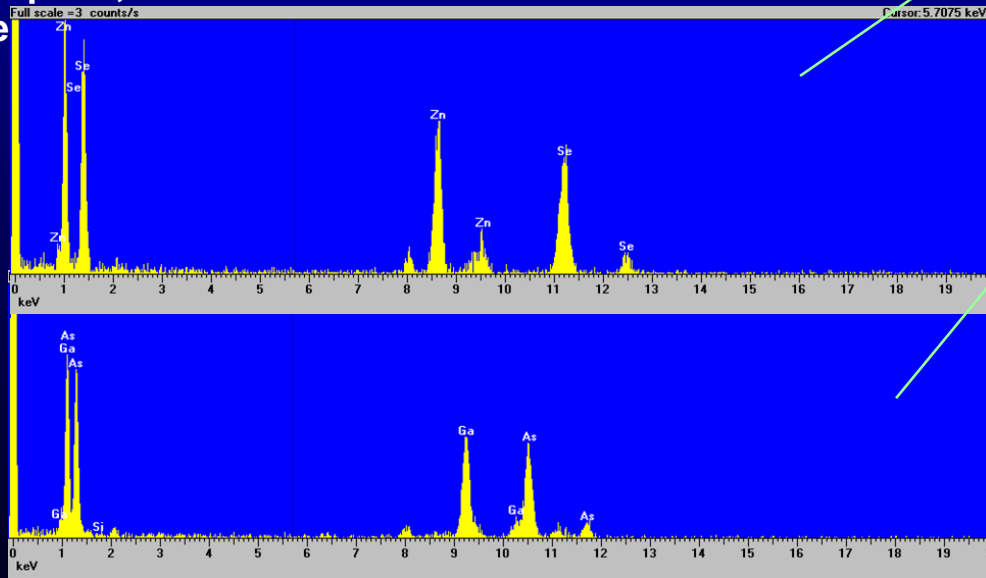


Selective area diffraction shows the expected (110) projection of electron



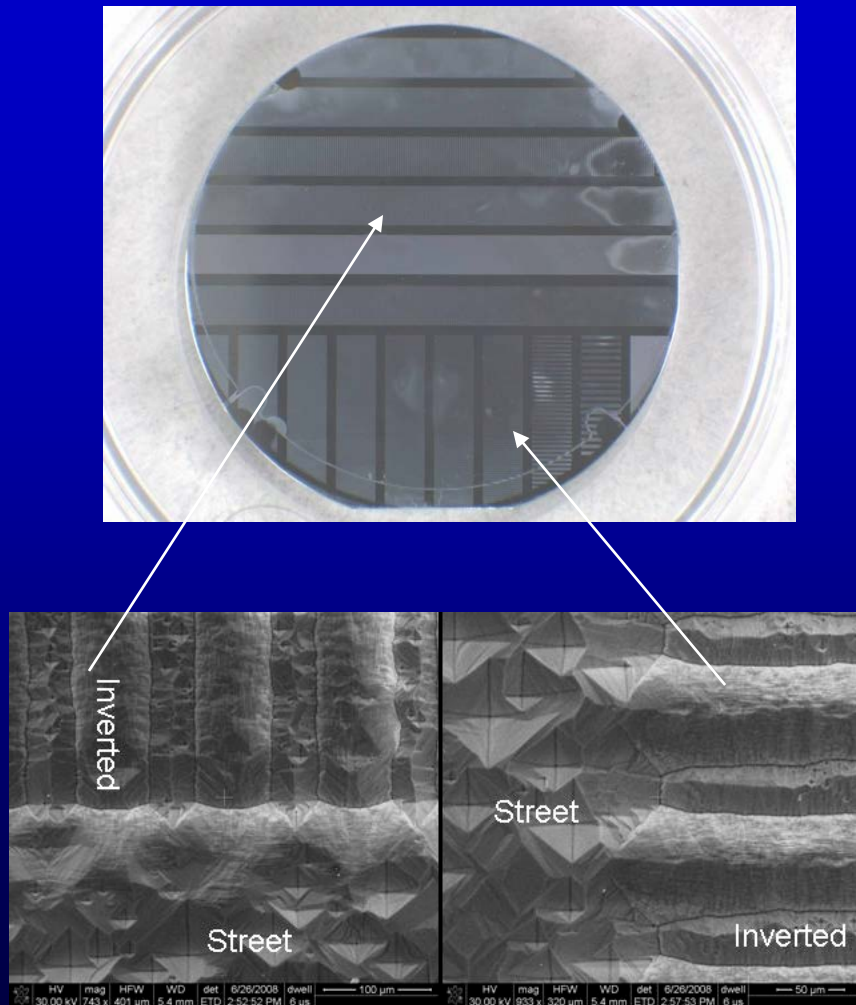
Cleaved (110) edge of grating reveals domain interfaces in SEM

High-resolution TEM shows epitaxial alignment of ZnSe film with beam GaAs template; line marks the interface



Energy dispersive X-ray analysis shows the Zn and Se, and Ga and As peaks above and below the substrate-film interface, respectively.

# SEM of (001) Shows Orientation Reversal in Morphology



- Morphology of individual domains switches as expected for gratings oriented perpendicular to each other



# Summary

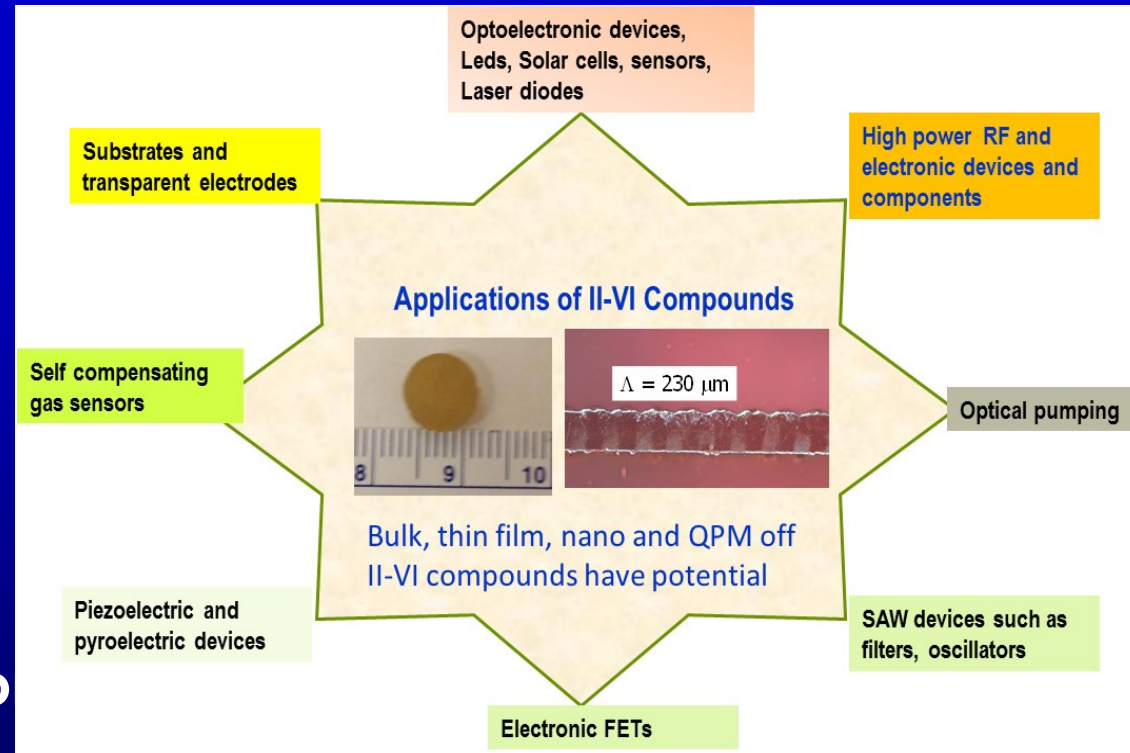
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- There is a strong need of material for MWIR and LWIR applications
- GaSe is an excellent materials, but suffers from cleavage plane.
- TAS is well developed, good for SHG applications. It has large walkoff angle.
- AgGaGeSe has great promise since it has better properties such as absorbance, transparency and no annealing or cracking compared to that of AgGaSe<sub>2</sub> and ZnGeP<sub>2</sub> crystals
- GaSe and ZnSe are excellent materials for THz sensor



# ZnSe is a multifunctional material

- ZnSe is a unique material
- Flight experiment is scheduled for PVT growth
- We have grown  $\text{ZnSe}_x\text{S}_{1-x}$  crystals to tailor the properties
- We have studied its transmission, emission and absorption characteristics
- We are continuing because of wide range of applications



With increasing concentration of S, quality of  $\text{ZnSe}_x\text{S}_{1-x}$  decreased